PCDD/FS IN AMBIENT AIR AT THE WORLD TRADE CENTER

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Introduction

On September 11, 2001, two commercial airliners crashed into the World Trade Center in New York City. Both planes were loaded with an estimated 90,000-L of jet fuel, as both were in route to the West Coast. The estimated temperature of the resulting fire was 1000 degrees C. The Twin Towers were built in the 1970s, and both contained extensive plastics as well as electrical wiring and equipment. Analysis of air samples taken during the fire show Aroclor patterns, indicating there may have been Aroclor mixtures in the buildings. All of these materials are known to produce dioxins and furans during combustion.[1] The resulting fire burned for three months and was finally extinguished in December. The smoke plume engulfed the area surrounding the site now known as Ground Zero, and left ash covering a large portion of lower Manhattan. The air quality was measured at over a dozen sites by several agencies. The results presented here were taken from two high volume air samplers located approximately six blocks away from the site.

Beginning one month after the collapse of the World Trade Center in New York City and continuing for six months, the EPA Region VII Laboratory, in cooperation with the EPA National Exposure Research Laboratory and EPA Region II, analyzed over 130 samples from two sites near Ground Zero. Data from early samples were dominated by furans, especially TCDF, as one would expect of a combustion process. Once the fire was extinguished, the ratio of dioxins to furans shifted toward the dioxins with OCDD now the dominant contaminant. The Dioxin Toxic Equivalent (TEQ) decreased rapidly to trace values in final samples. A comparison of data from the two sites, one located 6 blocks east of the World Trade Center site (Site E), and one six blocks north (Site N), show wind direction played a crucial part in distribution of the contaminants.

The typical PCDD/F pattern produced by combustion of materials including chlorinated products reported in literature is that the furan/dioxin ratio (w/w) is greater than 1; the weight distribution of the homologues increases with increasing degree of chlorination for PCDDs, but shows a maximum at PeCDF or HxCDF for PCDFs, and the congener pattern contains almost every congener.[2] The ambient PCDD/F pattern is dominated by higher chlorinated PCDD, especially OCDD. Although these samples were clearly from a combustion process, they did not show the typical combustion pattern, especially in regards to a larger contribution of furans.

Methods and Materials

Samples were collected using PS-1 samplers fitted with glass fiber filters and polyurethane foam (PUF) cartridges. Samples were collected over 72-hours, with average air volumes of 1000 m^3. Samples were extracted and analyzed according to EPA Method 1613 as follows: Each sample, a glass cartridge containing PUF and filter, was spiked with 15 C_{13}-labeled dioxins and furans and soxhlet

extracted with Methylene Chloride for 16 hours. The extracts were concentrated and underwent multi-layered silica gel and acidic alumina clean-up. The samples were analyzed by HRGC/HRMS on a Micromass AutoSpec Ultima with Agilent 6890 GC equipped with splitless injection and 60 m DB-5 column. The MS was operated at 10,000 resolution under positive EI conditions.

Results and Discussion

Figure 1 shows the normalized distribution of the individual compounds in relation to the total at Site E. The furans are shown as solid bars, while the dioxins are patterned. The initial samples have a furan:dioxin ratio greater than the final samples, with those in late October and early November nearing the expected 1. The figure also shows that almost every isomer is present in the initial samples. The dioxins increase with increasing chlorination and the furans maximize in the PeCDF and HxCDF range. While all samples are dominated by OCDD and HpCDD, the early samples show a significant contribution of tetra-, penta-, and hepta-furans. The higher value of 1234678HpCDF is due to an interference with that compound. Gradually the pattern shifts to the final samples, which show domination by OCDD, with much larger contributions from the dioxins than furans. Although not pictured, Site N shows less furan dominance and a quicker move to OCDD dominance, and even more pronounced contribution of dioxins over furans at the end of the sampling period. By Jan 1, 2002, the concentration of TCDF leveled off to approximately 0.01 pg/m3, accounting for only about 1 % of the total PCDD/F. OCDD, however, began as about 20 % of the total, and ended well over 50 %. TCDD was not detected in samples after December 3, and never contributed more than 1 % to the total value. While there is still some work being done at the site, there appears to be much less fire-related PCDD/F released into the air.

Figure 2 shows the total PCDD/F found at both sites as a function of time. The total at Site E began in October at 78 pg/m3, dropped significantly in early November to less than 20, and by January was less than 1. At Site N, the total in October varied considerably, maximizing over 20 pg/m3, but generally less than 5. By December, the total was also less than 1pg/m3. The prevailing winds have directed much more of the smoke plume over Site E than Site N, especially in September and October. Most pictures of Ground Zero show the smoke moving east or south, and wind direction measurements from New York confirm this trend. This explains the differences in the data from the two sites. This also explains spikes in the data seen on several days during sampling. The normalized distribution of individual compounds at Site N shows less of a combustion pattern in the beginning of the analysis, confirming that smoke did not accumulate north of Ground Zero. Wind data shows that beginning in November, the smoke plume and later ambient air was generally directed away from both sites, explaining the drop off in total values and furan contributions to that total.

The TEQ is based on TEF=s obtained from the WHO 1997 study[3], using one half the MDL (Method detection limit based on 40 CFR part 136 Appendix B) times the TEF for values below the MDL (which would result in a TEQ of 0.016 for a sample with no detected PCDD/F). Beginning in October, the TEQ was 7.1 pg/m3 at Site E and only 1.7 at Site N. But by late October, the value at Site E had already dropped to just over 3, and by the end of November, the Site E TEQ was 0.15 pg/m3. Site N had one spike back to 2 pg/m3, but generally was less than 0.5 for the duration of the project. Final measurements are only slightly higher than the field blanks shipped with the samples which average 0.16 pg/m3.

In conclusion, the air samples collected surrounding the World Trade Center site confirm the presence of dioxins and especially furans resulting from the intense fire. The later samples show that once the fire was extinguished, the concentrations greatly decreased, and are now at levels one would expect for ambient air.

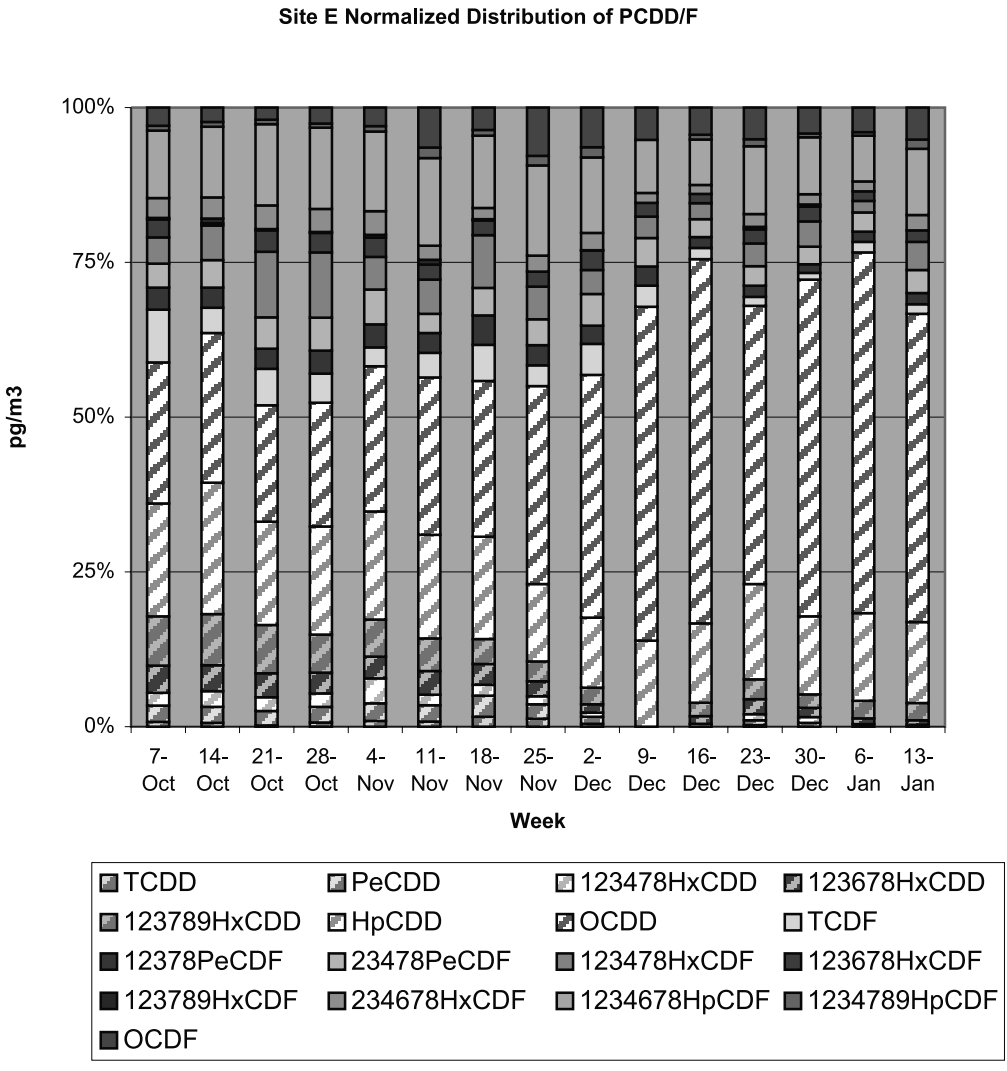

Figure 1.

Acknowledgments

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References

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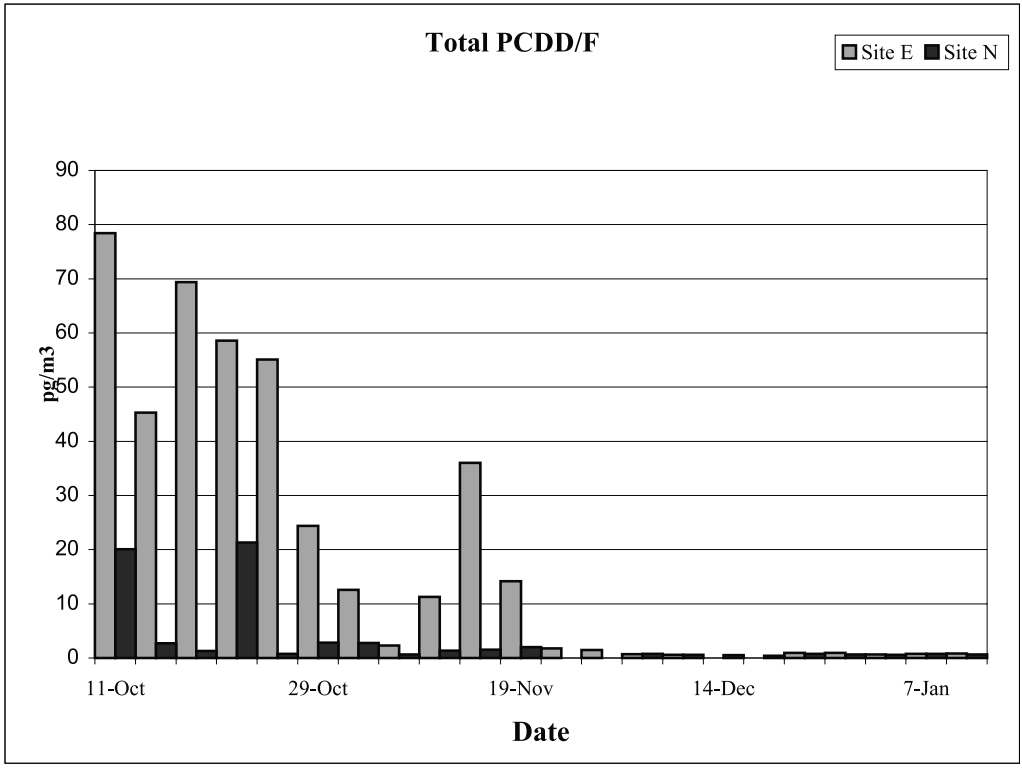
Total PCDD/F
Site E
Site N
pg/m3
90
80
70
60
50
40
30
20
10
0
11-Oct
29-Oct
19-Nov
14-Dec
7-Jan
Date

Figure 2.